1.1 Introduction

Spiegelman et al. (2000) proposed a calibration method called parallel calibration. McClure (1987) and McClure et al. (1987) introduced the Q-matrix method as a calibration technique. Upon examining these references it is obvious that parallel calibration is the same technique as the Q-matrix method. We show, using straight forward matrix algebra, that parallel calibration, and thus the Q-matrix method, is also equivalent to principal component regression using all components and generalized inverse regression. Discussions of principal component regression (pcr) applied to multivariate calibration problems can be found in Martens and Naes (1989) or Haaland and Thomas (1988). We argue that parallel calibration is an inefficient way to perform principal component regression because most often one would not want to use all components.

Section 2 sets notation and presents matrix results. In section 3 the equivalence between parallel calibration and pcr is shown and in section 4 the equivalence between generalized inverse regression and parallel calibration is shown. Section 5 summarizes the results.

1.2 Notation

We use notation that is consistent with Spiegelman et al. (2000). Let c be an $n \times 1$ vector of known concentrations and let Y' be an $n \times q$ matrix of n independent

spectra. The prime symbol denotes the transpose of a matrix or a vector. The ith row of Y' is the $1 \times q$ vector y_i'. Assume that $n < q$ so the rank of Y' is n.

To show that parallel calibration is equivalent to pcr, the spectral representation of the symmetric matrices YY' and $Y'Y$ and the singular value decomposition (SVD) of Y' are needed, see Christensen (1996, Sec. 14.5). The matrices YY' and $Y'Y$ share the same n positive eigenvalues, $\sigma_1^2, \ldots, \sigma_n^2$. Let $D(\cdot)$ denote a diagonal matrix and let

$$\lambda_i = \begin{cases} \sigma_i^2 & \text{for} \quad i = 1, \ldots, n \\ 0 & \text{for} \quad i = n+1, \ldots, q. \end{cases}$$

The spectral representation of YY' gives

$$YY' \;=\; P\, D(\lambda_i)\, P' \;=\; [P_1, P_2]\, D(\lambda_i)\, [P_1, P_2]' \;=\; P_1\, D(\sigma_i^2)\, P_1'.$$

where P is a $q \times q$ matrix with columns that are orthonormal eigenvectors of YY'. P_1 contains the first n columns of P and P_2 the remaining $q - n$ columns. Similarly,

$$Y'Y = Q\, D(\sigma_i^2)\, Q'$$

where Q is a $n \times n$ orthogonal matrix with columns that are orthonormal eigenvectors of $Y'Y$. Finally

$$Y' = Q\, D(\sigma_i)\, P_1'.$$

1.3 Principal Component Regression

Upon observing a new spectra measurement z, Spiegelman et al. (2000) suggest minimizing $\| z - A(y_1, \ldots, y_q) \|$ with respect to linear operators from $R^{n \times q}$ to R^q.

The operator that minimizes this norm can be written as

$$\hat{A} = (Y'Y)^{-1}Y'z.$$

The predicted concentration corresponding to the new spectra measurement z is

$$\begin{aligned} \hat{c}_z \;=\; \hat{A}'c &= z'Y(Y'Y)^{-1}c \\ &= z'(P_1 D(\sigma_i)Q')\,(QD(\sigma_i^2)Q')^{-1}c \\ &= z'P_1 D(\sigma_i)Q'\,QD(1/\sigma_i^2)Q'c \\ &= z'P_1 D(1/\sigma_i)Q'c. \end{aligned} \tag{1.1}$$

Now we show that pcr gives the same prediction. Consider fitting the following linear model to the observed concentrations,

$$c \;=\; Y'\beta + e, \quad E(e) = 0, \quad cov(e) = \sigma^2 I. \tag{1.2}$$

I is an $n \times n$ identity matrix. Because the rank of Y' is $n < q$ the matrix YY' does not have an inverse and there is not a unique least squares estimate of β. Principal component regression is a technique that replaces the original variables in Y' with a smaller set of new variables, say U', that are linear combinations of the original variables. The cross-product matrix UU' will have an inverse. Estimation and prediction is performed using the transformed variables. See Christensen (1996), Martens and Naes (1989), or Joliffe (1986) for a more complete discussion of pcr.

The variables in $U' = Y'P_1$ are referred to as principal components and U' is $n \times n$

with rank n. Regressing c on U' leads to the pcr model,

$$c = U'\gamma + e, \quad E(e) = 0, \quad cov(e) = \sigma^2 I.$$

The ordinary least squares estimate of γ is

$$\begin{aligned}
\hat{\gamma} &= (UU')^{-1}Uc \\
&= (P_1'YY'P_1)^{-1}P_1'Yc \\
&= (P_1'(P_1D(\sigma_i^2)P_1')P_1)^{-1}P_1'\,(P_1D(\sigma_i)Q')c \\
&= D(1/\sigma_i)Q'c.
\end{aligned}$$

Because the estimate of γ is based on transformed spectra, for a new spectra measurement z prediction is based on the transformed spectra $w' = z'P_1$.

$$\begin{aligned}
\hat{c}_{pcr} &= w'\hat{\gamma} \\
&= (z'P_1)\hat{\gamma} \\
&= z'P_1D(1/\sigma_i)Q'c,
\end{aligned}$$

which is identical to (1.1). This shows that predictions from the parallel calibration method and from pcr are identical when eigenvectors corresponding to all the positive eigenvalues are used to transform the spectra matrix in pcr. Often pcr is performed dropping components that correspond to small σ_i^2 values.

1.4 Generalized Inverse Regression

Marquardt (1970) suggested estimating β in equation (1.2) with $\hat{\beta} = (YY')^{+}Yc$, where $(YY')^{+}$ is the Moore-Penrose (M-P) generalized inverse of YY'. Using this estimate of β for predictions is referred to as generalized inverse regression. The predicted concentration for spectra measurement z is then

$$\hat{c}_m \;=\; z'\hat{\beta} \;=\; z'(YY')^{+}Yc.$$

It is easily shown that $(YY')^{+} = P_1\, D(1/\sigma_i^2)\, P_1'$. If $(YY')^{+}Y = Y(Y'Y)^{-1}$ then predictions from parallel calibration and generalized inverse regression will be identical. This is well known, see Harville (1997, Theorems 20.5.4 and 20.6.1) or Strang (1988, pp. 443-452 and homework problem A.6 (b)), but for clarity this equality is reestablished here.

Using the SVD of Y and the spectral representation of $Y'Y$ we can write

$$\begin{aligned}
(YY')^{+}Y &= (P_1 D(\sigma_i^2) P_1')^{+} (P_1 D(\sigma_i) Q') \\
&= (P_1 D(1/\sigma_i^2) P_1')\, (P_1 D(\sigma_i) Q') \\
&= P_1 D(1/\sigma_i) Q' \\
&= Y(Y'Y)^{-1}.
\end{aligned}$$

An alternative, but similar, proof that pcr and generalized inverse regression are the same can be found in Christensen (1996, pp 366-369).

1.5 Summary

We have established that parallel calibration is equivalent to pcr when eigenvectors corresponding to all n positive eigenvalues are used to transform the spectra Y'. In fact, we believe this is an inherent weakness of parallel calibration. If, for example, the smallest positive eigenvalue was 10^{-8}, then predictions from parallel calibration would be forced to use the eigenvector associated with this extremely small positive eigenvalue. A discussion of the implications for prediction when principal components corresponding to small eigenvalues are included in a regression can be found in Christensen (1996) or Joliffe (1986).

In our opinion, users of pcr should evaluate how useful a variable is before including that variable in a prediction equation; analysts should not simply choose to use eigenvectors corresponding to all n positive eigenvalues, as parallel calibration does. Joliffe (1986) discusses several methods for choosing which eigenvectors to include in regression.

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